

TITLE: Radically New Adsorption Cycles for Carbon Dioxide Sequestration

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## 1. ABSTRACT

### Introduction and Objectives

It is now generally accepted by most climate scientists that increasing global temperatures over the last 50 years are the result of increased atmospheric concentrations of greenhouse gases such as methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O) and, most especially, carbon dioxide (CO<sub>2</sub>). Of the known ways to manage the emission of greenhouse gases, the idea of carbon sequestration is probably the newest means being studied to manage carbon in the environment. In this option carbon dioxide is captured and securely stored for long-term sequestration. The most likely options for CO<sub>2</sub> separation and capture include (1) chemical and physical absorption, (2) physical and chemical adsorption, (3) low-temperature distillation, (4) gas separation membranes, and (5) mineralization. Among these, physical absorption using amines is currently the most widely deployed commercial technology. However, there is a significant energy penalty associated with this technology from the heat required to regenerate the solvent. That is why this project involves the exploration of radically new pressure swing adsorption (PSA) cycles for complete separation of CO<sub>2</sub> from coal gasification off gas streams at elevated temperatures, even though adsorption technology has been recently frowned upon for CO<sub>2</sub> capture.

For example, an International Energy Agency study evaluated CO<sub>2</sub> separation and capture using an adsorption system employing 13X zeolite as the adsorbent and both PSA and temperature swing adsorption (TSA) operational modes and concluded that these technologies are not attractive to the gas- and coal-fired power systems. This conclusion has led many to extrapolate the findings and conclude that adsorption systems, in general, are not applicable for CO<sub>2</sub> separation and capture. It is strongly suggested here that this is not true! It is true that the commonly studied adsorbents (e.g., zeolites and activated carbons) suffer from low capacity at elevated temperatures. However, there are some new adsorbents, generally referred to as hydrotalcite-like compounds (HTLcs) that are selective to CO<sub>2</sub> at elevated temperatures and release it simply by changing the pressure.

Therefore, the objective of this short one-year scoping research project is to develop both simple and rigorous mathematical models to predict the performance of two new PSA cycles, referred to as enriching reflux (ER) and dual reflux (DR) PSA, and one more traditional (but high temperature) PSA cycle, referred to as stripping reflux (SR) PSA. The results from these simple (isothermal, equilibrium) models and rigorous (non-equilibrium, non-isothermal) models will be compared to each other to evaluate their performance and potential for efficiently concentrating CO<sub>2</sub> from high temperature gas streams using hydrotalcite type adsorbents.

#### Accomplishments to Date

During the current period of performance, the isothermal equilibrium models for ER and DR PSA have been developed and a parametric study has been performed with the ER PSA model using an adsorption isotherm for CO<sub>2</sub> on a hydrotalcite from the literature. This ideal feasibility study revealed interesting thermodynamic limitations of ER PSA for CO<sub>2</sub> recovery from flue gas streams. A simple ER PSA cycle can produce very high purity CO<sub>2</sub> at high recovery using moderate conditions. However, ER PSA may exhibit low throughputs, depending on the adsorbent selectivity and feed concentration of CO<sub>2</sub>. ER PSA may also experience high pumping costs associated with high desorption flows, which are related to the adsorbent selectivity and feed concentration of CO<sub>2</sub>. This work by Ebner and Ritter (2004) has been submitted recently to *Adsorption* for review and consideration for publication. A follow-up study will compare the performance of an SR PSA cycle with those of similar ER and DR PSA cycles, under ideal, isothermal, equilibrium conditions.

Also, during the current period of performance, the non-equilibrium, non-isothermal models for ER and DR have been developed and are currently undergoing validation. Now that the rigorous ER and DR PSA codes have been developed, a recent effort has been to modify the existing rigorous SR PSA code for the proposed high temperature PSA cycle utilizing a hydrotalcite adsorbent (from the literature) to concentrate CO<sub>2</sub> at high temperature. A parametric study with the SR PSA code will soon be underway. Overall, it is anticipated that if not ER PSA, soon to be studied, SR PSA may compete very well against other technologies for CO<sub>2</sub> capture at high temperature, especially with the concurrent development of a viable high capacity HTLc compound.

For example, during the current period of performance, N. D. Hutson et al. (2004) (project collaborator from the EPA) prepared the following abstract for a manuscript submitted recently to *Chemistry of Materials*. The high temperature adsorption of CO<sub>2</sub> on Mg-Al-CO<sub>3</sub> hydrotalcite-like compound is affected by structural changes that take place upon heating of the material. The structural changes of a synthetic hydrotalcite upon heating to 200°C and 400°C in a vacuum were characterized using various analytical techniques. These structural changes were then related to observed behavior with respect to the physisorption and chemisorption of CO<sub>2</sub> at 200°C. Upon heating to 200°C, the material retains its layered structure, though the interlayer spacing is decreased by ~ 1 Å due to the loss of interlayer water. Chemisorption of CO<sub>2</sub> at 200°C represents more than half of the total adsorption capacity (at 107 kPa) due to increased availability of the framework Mg<sup>2+</sup> cation and the subsequent formation of MgCO<sub>3</sub>. There is no significant increase of surface area or pore volume after heating the material to 200°C. Upon heating to 400°C the CO<sub>3</sub><sup>2-</sup> in the interlayer is decomposed and it is suspected that the material is nearly completely dehydroxylated. The resulting amorphous 3-D structure with increased surface area and pore volume and decreased availability of the Mg<sup>2+</sup> cation favors physisorption over chemisorption for these samples.

#### Future Work

The work planned for the remaining months of this short one-year scoping research project includes the following tasks:

- carry out a follow-up study for publication on the performance of an SR PSA cycle with those of similar ER and DR PSA cycles, under ideal, isothermal, equilibrium conditions
- continue to develop the rigorous ER, DR and SR PSA models and carry out detailed parametric and comparison studies with them, and produce at least two (but probably three) manuscripts for publication
- generate substantial evidence for CO<sub>2</sub> capture by novel hydrotalcite based, high temperature PSA cycles to justify the continuation of this project with Phase II funding and then possible patent applications
- with the collaborator from the EPA, continue to develop a fundamental understanding of the behavior of HTlc compounds with respect to CO<sub>2</sub> capture and release, to provide insight into developing a material with superior performance
- with the collaborator from the EPA, continue to develop promising HTlc compounds that are more reversible, have a higher CO<sub>2</sub> working capacity and have faster kinetics (particularly desorption kinetics) than any material currently available

## 2. LIST OF PUBLISHED JOURNAL ARTICLES, COMPLETED PRESENTATIONS AND STUDENTS RECEIVING SUPPORT FROM GRANT

#### Journal Articles Under Review

- Nick D. Hutson, Scott A. Speakman and E. Andrew Payzant, "Structural Effects on the High Temperature Adsorption of CO<sub>2</sub> on a Synthetic Hydrotalcite," *Chemistry of Materials*, submitted April 2004.

- Armin D. Ebner and James A. Ritter, “New Enriching Reflux Pressure Swing Adsorption Cycle for Carbon Dioxide Sequestration,” Adsorption, submitted April 2004.

#### Conference Presentations

- Steven P. Reynolds, Sarang A. Gadre, Nick D. Hutson, Armin D. Ebner and James A. Ritter, “New Pressure Swing Adsorption Cycles for Carbon Dioxide Sequestration,” 8<sup>th</sup> International Conference of Fundamentals of Adsorption (FOA8), Sedona, AR, May 2004.
- N. D. Hutson, S. A. Gadre, A. D. Ebner and J. A. Ritter, “Separation and Capture of CO<sub>2</sub> using a High Temperature Pressure Swing Adsorption System,” Third Annual Conference of Carbon Capture & Sequestration, Alexandria, VA, May 2004.
- J. A. McIntyre, N. D. Hutson, A. D. Ebner and J. A. Ritter, “New Adsorption Technology for Carbon Dioxide Sequestration,” AIChE 2003 Annual Meeting, San Francisco, CA, November 2003.
- J. A. McIntyre, N. D. Hutson, A. D. Ebner and J. A. Ritter, “New Adsorption Technology for Carbon Dioxide Sequestration,” 13<sup>th</sup> Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, Tennessee, October 2003.

#### Students Supported Under this Grant

- James A. McIntyre, PhD, May 2003, Department of Chemical Engineering, University of South Carolina. Thesis title: Theoretical and Experimental Analyses of Novel Pressure Swing Adsorption Cycles for Heavy Component Enrichment. After defending his PhD, James stayed on for a few months before joining 3V, Inc. and initiated the development of the ER and DR PSA computer codes for the high temperature adsorption cycles. His support came from a MeadWestvaco Fellowship.
- Sarang A. Gadre, PhD, June 2003, Department of Chemical Engineering, University of South Carolina. Thesis title: Experimental Design and Simulation of a Metal Hydride Hydrogen Storage System. Sarang, now a Postdoctoral Associate in my group and being supported partially by this grant and a MeadWestvaco Fellowship, is working with Steven on PSR code development, in particular on the DR PSA code.
- Steven P. Reynolds, PhD graduate student, Department of Chemical Engineering, University of South Carolina. Steven, while being supported through an NSF K-12 Graduate Fellowship, is working with Sarang on PSA code development, in particular on the SR and ER PSA codes and also on the design of a high temperature SR, ER or DR universal PSA system to be built if continued funding is obtained.